Techniques for Structural Characterization of Amorphous Materials and an Application to Diatoms

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Techniques for Structural Characterization of Amorphous Materials and an Application to Diatoms

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Abstract - Amorphous materials as well as crystals are important for understanding environments on the earth. However, the techniques for structural characterization of amorphous materials are not well known in the domain of environmental science. X-ray diffraction, EXAFS, IR and Raman spectroscopy are useful for these purposes. Merits of each technique and an application for structural analysis of amorphous diatoms are mentioned in this paper.

I Introduction

The earth crust is made of many kinds of crystalline materials (minerals). The structural information of minerals is important for understanding many geological events such as the formation, displacement and deformation of rocks, the transformation of minerals and mechanism of earthquake.

On the other hand, on the surface of the earth, there are many kinds of non-crystalline materials as well as crystalline materials. For example, we can find easily various non-crystalline materials such as volcanic glasses, microorganism and biogenic materials. Therefore, the structural information of these non-crystalline materials give clues to elucidate biomineralization processes and various interactions between water and soils. However, these non-crystalline materials have been out of the range of scientists in the domain of environmental geology.

In this paper, several techniques for structural characterization of amorphous materials (X-ray diffraction measurements, EXAFS spectroscopy, IR and Raman spectroscopy) will be introduced. It is also explained what kind of information can be obtained by these techniques. Further, an application of IR spectroscopy for characterization of non-crystalline diatom frustules is introduced as an example.

II. Techniques for structural characterization of amorphous materials

The structure of crystalline materials can be shown by the positions and temperature factors of the atoms in a unit cell. The structural information could be determined by the X-ray diffraction techniques, exactly. However, the analytical technique to determine the structure of non-crystalline materials such as glasses and liquids is not established yet. Therefore, only reliable model structures for non-crystalline materials can be obtained by means of various characterization techniques.

The structure of non-crystalline materials may be classified to 1) short-range structure, 2) medium range structure and 3) long-range structure (texture).

1) Short-range structure means the structure that include an atom and its first-neighboring atoms in the region of $r < 0.3$ nm. This structure is controlled by atomic pair distance, coordination number, etc. and can be determined by diffraction technique (X-ray, neutron and electron), X-ray spectroscopy (EXAFS), and Raman and infrared spectroscopy [1-4].
2) Medium-range structure related with the linkage of short-range structures in the range of $r<1.0$ nm. For example, the linkage structure of SiO_4 tetrahedra in the silicate glass such as 3, 4, 6 and 8 member rings belong to this type structure. It is difficult to reveal medium-range structure in detail. However, a medium-range structure on a certain level can be obtained by X-ray diffraction and computer calculation techniques [1,5]
3) Long-range structure is the structure of scale of scores in nm, which includes several kinds of amorphous phase. This structure has been analyzed by small angle X-ray scattering (SAXS) and electron microscopic techniques [6].

In the following sections, several techniques for characterization of amorphous materials are mentioned to show merits of each technique.

A. X-ray diffraction method

X-ray diffraction method is very useful technique for characterization of the amorphous materials as well as crystalline materials. By this technique, we can obtained direct information of atomic arrangements of the amorphous materials.

The basic theory to determine the structure of non-crystalline materials based on the X-ray diffraction data was given by Zernike and Prins [7]. They presented the method to obtain electron radial distribution function by Fourier transformation of X-ray diffraction data. Warren, Krutter and Morningstar [8] applied this method to determine the structures of SiO_2 and B_2O_3 glasses. This technique is a standard method for structural characterization of non-crystalline materials.

Usually, pair correlation functions of atomic pairs in

amorphous materials are obtained by X-ray diffraction method. The basic structural unit of natural amorphous materials (for example, volcanic silicate glass) has nm scale structure, which can be analyzed using an X-ray with λ of about 0.1nm. The diffraction intensity of non-crystalline materials is shown by a following Debye's formula,

$$I(Q)=\sum_{i} f^2_i(Q) + \sum_{i}\sum_{i\neq j} f_i(Q)f_j(Q)\{\sin(Qr_{ij})/Qr_{ij}\} + I_{inc}(Q) \quad (1)$$

where r_{ij} is the distance between the i th and j th atoms, $f_i(Q)$ is the atomic scattering factor of i th atom, and $Q=4\pi\sin\theta/\lambda$. $I_{inc}(Q)$ is the intensity of the incoherently scattered X-rays. The second term of equation (1) is structure sensitive term. By Fourier transformation of second term, we can a pair correlation function (Radial distribution function). Fig.1 shows the X-ray diffraction intensity of SiO_2 glass [1]. The X-ray diffraction intensity of amorphous materials shows one or two broad peaks. Fig.2 show the radial distribution function of SiO_2 glass calculated from the observed intensity [1]. In Fig.2, the dominant peak at r=0.16nm is assigned to Si-O pair in SiO_4 tetrahedron. From the area under this peak, we can estimate the number of oxygen around Si atom (coordination number) as about 4. The peaks at r = 0.26 and 0.31nm are considered as O-O pair of SiO_4 tetrahedron and Si-Si pair between neighboring two SiO_4 tetrahedra. These results suggest that we can obtain some direct structural information by X-ray diffraction technique.

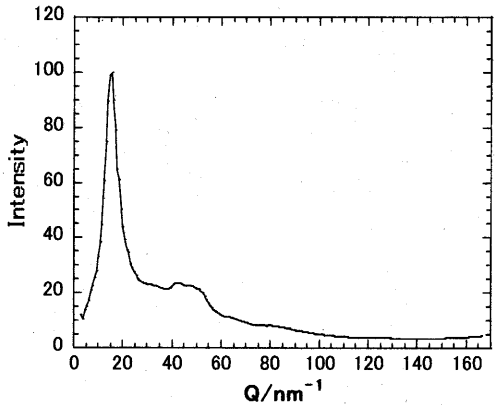

Fig.1 X-ray diffraction intensity of SiO_2 glass [1].

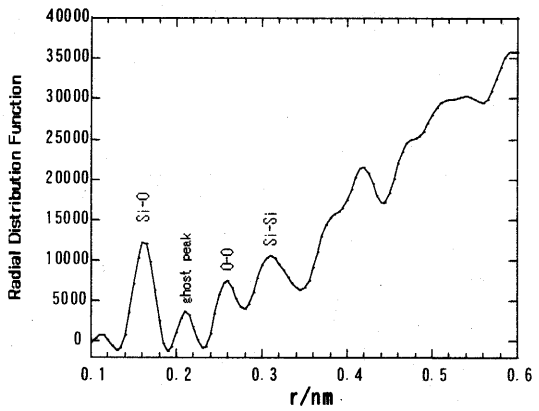

Fig.2 Radial distribution function of SiO_2 glass [1].

B. EXAFS spectroscopy

EXAFS (Extended X-ray Absorption Fine Structure) is an oscillatory structure that is observed on an X-ray absorption spectrum in the higher energy region than absorption edge. EXAFS originates from an oscillatory modulation of X-ray absorption due to the interference between out going photoelectron waves and incoming waves which are backscattered by atoms around an excited atoms (absorbing atom). From this EXAFS spectrum, we can obtain structural information around absorbing atom. This technique can apply to non-crystalline materials as well as crystalline ones. Since EXAFS can provide the information on the atomic distribution around an absorbing atom separately with other constituent atoms, it would be a powerful structural for structural analysis of amorphous multi-component system. For example, we can obtain a pair distribution around Si atom of SiO_2-Al_2O_3 glass from Si EXAFS spectrum.

Fig.3 shows Ge K absorption spectrum of GeO_2 compounds [9]. The EXAFS spectrum of GeO_2 glass is similar to that of the trigonal crystal (low-quartz type). This fact may indicate that GeO_2 glass has GeO_4 tetrahedra in the structure.

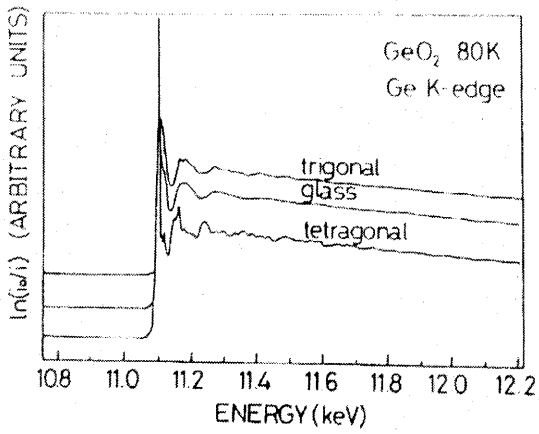

Fig.3 Ge K absorption spectra of GeO_2 compounds [9].

C. IR and Raman spectroscopy

IR spectroscopy is a technique for analysis of vibration of molecules of materials. Some parts of IR lights (λ = 1 - 50μm) radiated on a material are absorbed by the material. The wavelength and intensity of absorbed light depend on the composition and structure of the material. In other words, this technique gives information of conditions around a molecules as well as its existence Therefore, IR spectroscopy is very useful for identification, qualitative and quantitative analyses and molecular structure analysis of various materials. Especially, it is applied commonly to analyses functional groups in organic materials. However, this technique is also useful for structural analysis of non-crystalline materials [4].

Fig.4 shows IR spectra of fused SiO_2 glass (a-SiO_2) and low-quartz. The bands in the region ν = 900 – 1300 cm^{-1} for SiO_2 glass are commonly assigned to the asymmetric stretching vibrations of Si-O atomic pairs. The band at about

800 cm^{-1} is assigned to Si-O stretching in SiO_4 tetrahedra. The band at about ν = 500 cm^{-1} is assigned to Si-O-Si bending vibration. Comparing the spectrum of SiO_2 glass with that of low-quartz, the spectrum of SiO_2 glass shows broader absorption bands than those of low-quartz. For example, the width of intense bands at about 800 and 1100 cm^{-1} in SiO_2 glass is wider than that of low-quartz crystal. This fact may indicate that SiO_4 tetrahedra in the low-quartz crystal are more regular than those in SiO_2 glass. Therefore, the intensity and frequency of these bands give information of regularity of SiO_4 tetrahedra. As the absorption bands at about 500 cm^{-1} give the information of linkage of SiO_4 tetrahedra, the broadness in SiO_2 glass indicate the wide distribution of Si-O-Si bridging angle.

Raman spectroscopy is a technique based on a scattering of light by materials. This scattering is due to interaction between photons and molecules in materials. Therefore, Raman spectroscopy gives similar information of materials (molecular structures and chemical bonds) with those obtained by IR spectroscopy. Moreover, this technique has some advantages. For example, this technique has a higher space resolution (about 1 μm) than IR spectroscopy (about 10 μm) by using an optical microscope. Raman spectroscopy is also useful for structural analysis of amorphous materials as well as crystalline materials [3].

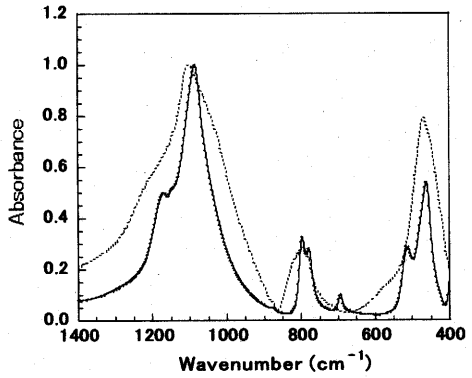

Fig.4 IR spectra of SiO_2 glass (dotted line) and low-quartz.

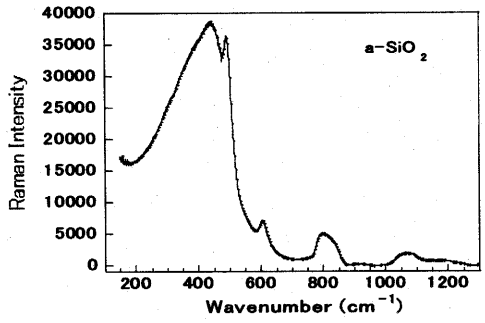

Fig.5 Raman spectrum of SiO_2 glass.

Fig.5 shows Raman spectrum of fused SiO_2 glass. On this spectrum, typical broad bands of amorphous materials are observed at around 455, 800, 1060 and 1200 cm^{-1} , onto which are superimposed two sharp bands at 490 and 600 cm^{-1}, the "defect" bands denoted D1 and D2 bands, respectively. Raman spectrum of SiO_2 glass has been extensively studied [10]. The major broad Raman band near ν = 450 cm^{-1} is inferred to involve mainly oxygen displacement and generally assigned to a symmetric oxygen vibration of the bent Si-O-Si linkages, with oxygen motion perpendicular the Si ... Si line. It is also accepted that sharp bands at ν = 450 cm^{-1} (D1) and 600 cm^{-1} (D2) correspond to the symmetric oxygen breathing vibration of four- and three-membered siloxane rings of SiO_4 tetrahedra, respectively, embedded as "defects" within the glass structure. The band at ν = 800 cm^{-1} is assigned to the Si-O stretching vibration with dominant Si motion. In the higher frequency region (ν > 900 cm^{-1}), weak Raman bands at about 1060 cm^{-1} and about 1200 cm^{-1} are assigned to asymmetric Si-O stretching vibrations. Based on these assignments of Raman bands, we can obtain structural information of amorphous SiO_2 materials with different structural states.

III. An application to diatoms

Diatoms are plankton of unicellular whose cell walls (exoskelton, frustule) are made of amorphous silica and organic materials [11]. Silica materials are important not only for industrial use, but also for understanding biomineralization processes. Therefore, the knowledge of nano-scale structure of diatoms are very important for searching new materials and understanding states of silica materials in the primitive life. An example of X-ray diffraction and IR spectroscopic study for the structure of diatom frustule is given in this section [11].

A. Specimen

Pennate diatoms were collected from acidic hot spring at Kamuiwakka Falls, Shiretoko Peninsula, Hokkaido, Japan [11]. Fig.6 is an optical micrograph of the pinnate diatom.

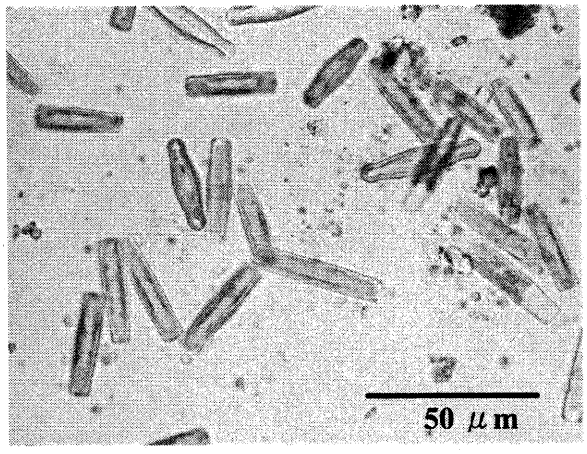

Fig.6 Optical micrograph of pennate diatom.

It shows broad linear valve and rectangular girdle bands. This figure reveals that long-axis of pennate diatom is about 30 μm in length. This diatom was analyzed by a scanning

electron microscope equipped by energy depressive X-ray analyzer (JEOL, JSM-5200LV). The analysis shows that exoskelton of diatoms are composed of large amount of Si with a little S.

B. X-ray powder diffraction analysis of diatoms

About 10mg of diatom samples was mounted on a Si plate that shows no Bragg diffractions. X-ray diffraction measurement was carried out on a powder X-ray diffractometer (Rigaku, RINT2200). A diffraction profile of vitreous SiO_2 was also measured as a reference material. Fig.7 shows obtained X-ray powder diffraction profile of diatom together with that of vitreous SiO_2. The profile of diatom shows only a broad peak around $2\theta=20^{\circ}$. This fact may indicate that diatoms are composed by amorphous SiO_2 materials. The profile of diatom is similar to that of vitreous SiO_2. However, there is a small difference between these two profiles. The intensity in the low 2θ ($<10^{\circ}$) of diatom is higher than that of the vitreous SiO_2. On the other hand, SiO_2 gel shows such small angle diffraction. Therefore, it is possible that microstructure of diatoms have small structural units with 10-100 nm scale.

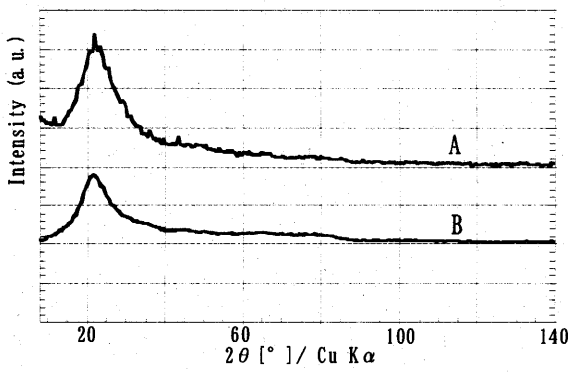

Fig. 7 X-ray diffraction profiles of the diatom (A) and vitreous SiO_2 (B).

C. IR spectroscopic study

IR spectrum of diatom was measured under a micro-FTIR system (JASCO FTIR-610) consisted of a FTIR spectrometer and an IR microscope (Fig.8).

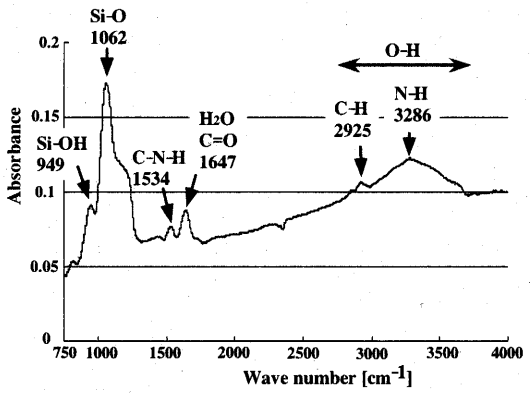

Fig.8 IR spectrum of pinnate diatoms.

The IR spectrum in the region of ν = 750-1400 cm^{-1} includes structural information of SiO_4 tetrahedra and their linkages. Comparing this spectrum with that of vitreous SiO_2 (Fig.4), the band intensity at ν = 800 cm^{-1} is weaker than those of low-quartz and vitreous SiO_2. Further, the spectrum of diatom shows another band at ν = 950 cm^{-1}. These bands are assigned to Si-O-Si bending and Si-OH stretching modes, respectively. These facts may indicate that diatoms have Si-OH bonds and the linkage of SiO_4 tetrahedra is lower than low-quartz and vitreous SiO_2. These features may be found in SiO_2 gel. This result is consistent with that of X-ray diffraction study.

References

[1] Y. Shimada, M. Okuno, Y. Syono, M. Kikuchi, K. Fukuoka, N. Ishizawa, "An X-ray diffraction study of shock-wave densified SiO_2," *Phys Chem Minerals*, Vol. 29, pp. 233-239, 2002.

[2] G.E. Jr. Brown, G. Calas, G.A. Waychunas, and J. Petiau, "X-ray absorption spectroscopy: Application in mineralogy and geochemistry," *Mineralogical Society of America Review in Mineralogy*, Vol. 18, pp. 431-512, 1988.

[3] M. Okuno, B. Reynard, Y. Shimada, Y. Syono, and C. Willaime, "A Raman spectroscopic study of shock-wave densification of vitreous silica," *Phys Chem Minerals*, Vol. 26, pp. 304-311, 1999.

[4] D. Niznansky, J.L. Rhespringer, "Infrared study of SiO_2 sol to gel evolution and gel aging," *J Non-Cryst Solids*, Vol. 180, pp. 191-196.

[5] M. Okuno, K. Kawamura, "Molecular dynamics calculations for $Mg_3Al_2Si_3O_{12}$ (pyrope) and $Ca_3Al_2Si_3O_{12}$ (grossular) glass structures," *J Non-Cryst Solids*, Vol. 191, pp. 249-259, 1995.

[6] T. Kakei, Y. Kameshima, A. Yasumori, K. Okada, N. Kumada, N. Kinomura, "SAXS analysis of texture formed by phase separation and crystallization of Al_2O_3-SiO_2 glasses," *J Non-Cryst Solids*, Vol. 282, pp. 265-277, 2001.

[7] F. Zernike and J.A. Prins, "The bending of X-rays in liquids as an effect of molecular arrangement," *Z. Physik*, Vol. 41, pp. 184-491, 1927.

[8] B.E. Warren, H. Krutter and O. Mornigstar, "Fourier analysis of X-ray patterns of vitreous SiO_2 and B_2O_3," *J Am Ceram Soc*, Vol. 19, pp. 202-206, 1936.

[9] M. Okuno, C.D. Yin, H. Morikawa and F. Marumo, "A high resolution EXAFS and near edge study of GeO_2 glass," *J Non-Cryst Solids*, Vol. 87, pp. 312-320, 1986.

[10] P.F. McMillan, B.T. Poe, PH. Gillet and B. Reynard, "A study of SiO_2 glass and supercooled liquid to 1950 K via high-temperature Raman spectroscopy," *Geochim Cosmochim Acta*, Vol. 58, pp. 3653-3664, 1994.

[11] R. Asada, M. Okuno and K. Tazaki, "Structural anisotropy of biogenic silica in pennate diatoms under Fourier transform polarized infrared microscopy," *J Mineral Petrol Sci*, Vol. 97, pp. 217-224, 2002.